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ANNUAL SUMMARY REPORT, 1 August 1980 - 31 July 1981

High Temperature Gas Energy Transfer

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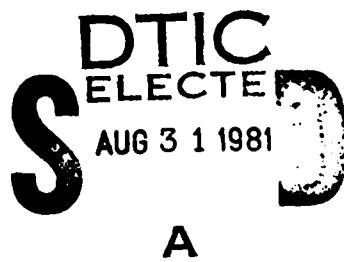University of Washington
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Diffusion Cloud Method	Thermal System
Energy Transfer	Transients
Gases	Variable Encounter Method
High Temperature	Vibrational Energy
	Wall Activation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Work under this contract is summarized. Five technical reports have been issued. The effect of molecular parameters — vibrational eigenstate density and intermolecular attractive potential — on gas-surface vibrational energy transfer — has been documented. The VEM technique has been refined to single collision measurements that provide a more sensitive test of energy transfer models. Study of cyclopropane to 1300 K shows a decline in collision efficiency with rise of temperature. Strong collision behavior is found at low gas-surface temperatures.

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I. <u>Summary of Progress</u>   This report covers the period 1 August 1980 –
31 July 1981. The statement below summarizes the most important results
and conclusions of the work in this period

1. Collisional efficiency in transfer of vibrational energy from a hot
molecule to a surface (or another molecule) declines with increase in vibra-
tional eigenstate density (i.e., with increase of number, and decrease in
frequency, of the number of internal vibrational modes) of the hot molecule.
However, paradoxically, the efficiency for collisional activation of reaction
increases with increase in eigenstate density of the substrate molecule.
These findings represent statistical effects and illustrate the statistical
theory of energy accommodation of Lin and Rabinovitch. These matters are
discussed in Technical Reports 16 and 17 for cyclopropane, methyl cyclo-
propane and cyclobutane, and include work in progress on cyclopropane-d_6.

2. In the higher temperature region, up to the highest temperature so far
investigated, 1325 K, the following results are found and conclusions con-
firmed: a) Collisional efficiency for vibrational energy transfer declines
with increase of temperature of the heat bath or surface acting as collision
partner (TR17, TR18); b) the decline in efficiency is most marked at lower
temperatures (below 1000 K) and itself decreases above that temperature (TR19).
Unfortunately, the general behavior for polyatomics in the region 1000-2000 is,
however, still a closed book even though such knowledge is essential for the
understanding and design of combustion, shock, laser, etc. systems. The model
for energy transfer — attractive interaction with statistical accommodation,
as opposed to a repulsive interaction and an impulsive phenomenon — may change
in this region.

3. The ordinary surface of flame and combustion systems behaves as a strong
collider for vibrational energy transfer involving polyatomic molecules (TR18)
at low temperatures ($\gtrsim$ 450 K).

4. The Variable Encounter Method (VEM) has been refined to single-collision
conditions. These are the first studies of single collisional activation of
reacting polyatomic molecules (by energy transport, <u>not</u> <u>catalysis</u>). The method
provides a much more refined probe of the form of the collision transition
probability matrix elements p_{ij} (TR20).

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II. Complete listing of Technical Reports:

1. Technical Report TR01, 7 January 1976.

   Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures by B. S. Rabinovitch, D. G. Keil, J. F. Burkhalter and G. B. Skinner.

   In this report a theoretical analysis was given of shock tube data for high temperature gas reactions. The data were analyzed to show that collisional energy transfer efficiency appears to decrease at high temperatures.

2. Technical Report TR02, 20 April 1976

   Temperature Dependence of the Arrhenius Activation Energy. High Temperature Limit, J. F. Burkhalter and B. S. Rabinovitch.

   In this report a conventional approximation to the high temperature vibrational partition function is shown to be defective, and the usual high temperature expression for the Arrhenius activation is in error. The variation of the activation energy for unimolecular reactions as a function of temperature is calculated for various representative systems.

3. Technical Report TR03, 15 October 1976

   Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems, D. C. Tardy and B. S. Rabinovitch.

   This report gives a comprehensive and detailed survey and analysis of energy transfer in thermal gaseous systems. The present status of the field is delineated and future areas of work indicated.

4. Technical Report TR04, 15 April 1977

   On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations, S. E. Stein and B. S. Rabinovitch.

   This report describes an algorithm for accurate state sum and density calculations and refutes an error in the literature.

5. Technical Report TR05, 15 August 1977

   Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems by I. Oref and B. S. Rabiovitch.

   In this report a simple theoretical model describing energy transfer probabilities is given. Conservation of angular momentum was imposed. The importance of completeness and detailed balance conditions and correction of an earlier model in the literature are illustrated. The model is applied to experimental data.

6. Technical Report TR06, 1 September 1977

Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method by D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch.

A theoretical and experimental study was made of flow and diffusion of a reactant in a low pressure gas stream. Connection is made with earlier theoretical analysis.

7. Technical Report TR07, 10 October 1978

Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically? I. Oref and B. S. Rabinovitch.

The literature is surveyed and analyzed. A variety of excitation techniques including crossed molecular beam, laser, chemical activation, photochemical and thermal are considered. The answer to the title question is "yes." The relationship to the present work on intermolecular transfer is the following: multiphoton laser experiments frequently involve collisional heating of the gas. In order to understand the results, one must have a good basis for interpretation of data. In this survey, some suggested models for energy relaxation by molecular collisions are criticized and data reinterpreted in light of results obtained in this laboratory.

8. Technical Report TR08. 1 November 1978

Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane. E. Kamaratos, J. D. Burkhalter, D. G. Keil and B. S. Rabinovitch.

A study of vibrational energy transfer by the Diffusion Cloud Method has been made at temperatures from 975 K to 1175 K in the cyclopropane isomerization system. H_2, He, N_2 and CO_2 were studied as inert bath gases. Their relative efficiencies increase in that order. Values of $<\Delta E>$ vary from 150 cm^{-1} to 1100 cm^{-1} at 975 K. It was shown that these values decline, and the collisional efficiencies, β_c, decrease markedly with rise of temperature to 1175 K. This is only the second measurement of such a phenomenon.

9. Technical Report TR09. 15 March 1979

Collisional Relaxation of Non-Equilibrium Vibrational Energy Distributions in a Thermal Unimolecular System. Surface Collisions. D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch.

A novel, simple technique, the Variable Encounter Method, is described for obtaining information on energy transfer efficiency between a gas and a solid in the transient region, and as a function of temperature. The method is as powerful as it is simple. Results for cyclopropane are described. Decrease

in collisional efficiency $<\Delta E>$ with rise of temperature is confirmed, and the form of the transfer probability matrix $\underline{P}$ is discovered. This method and these results are considered to be some of the most innovative and important that have ever been made in this field.

10. Technical Report TR10. 15 June 1979

   Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures by VEM. M. C. Flowers, D. F. Kelley, F. C. Wolters, and B. S. Rabinovitch.

Extension of the VEM technique to cyclobutane is described. An exponential form of $\underline{P}$ is required to fit the data. The value of $<\Delta E>$ declines with rise of temperature.

11. Technical Report TR11; 15 September 1979

   Collisional Relaxation of Transient Vibrational Energy Distributions in a Thermal Unimolecular System. The Variable Encounter Method. D. F. Kelley, L. Zalotai and B. S. Rabinovitch.

The Variable Encounter Method permits the study of the transient in the relaxation of an initial vibrationally cold ensemble of molecules in a vibrationally hot distribution by a known and variable number of successive collisions with a hot wall. The system studied was the isomerization of 1,1,cyclopropane-d_2 with a fused quartz wall temperature of 800 K to 1175 K, and average number of collisions from 2.3 to 22.3. The detailed theory of the experiment was presented, together with the method of data deconvolution. Various modified gaussian and exponential models of energy transfer were found to give agreement with the data. The average down-step size was found to decline from ≤ 3500 cm^{-1} at the lowest temperature to ~ 2500 cm^{-1} at the highest on the basis of a gaussian model, but heterogeneous energy transfer is more efficient than homogeneous gas-gas collisional transfer. A mathematical analysis of the relation between mean first-passage times and incubation times is given. Incubation times increase from ~ 7 to ~ 12 collisions with increasing temperature. Transient population distributions and the sequential reaction probabilities as a function of collision number are calculated.

12. Technical Report TR12. 10 October 1979

   Vibrational Energy Transfer in a Diffusion-Flow Cyclopropane-d_2 System. J. F. Burkhalter, E. Kamaratos, and B. S. Rabinovitch.

In this study, absolute rate constants for isomerization of cyclopropane-d_2 and high temperature homogeneous energy transfer were determined in a diffusion-flow system. The relative rates of the competitive isotopic isomerization channels

were measured for two bath gases, N_2 and He, at two temperatures, 973 K and 1073 K. Values of the average energy down-jump size $<\Delta E>$ were computed from both the absolute rates and the isotopic relative rates by suitable modelling by a stochastic calculation. The results confirm earlier diffusion cloud measurements.

13. Technical Report TR13, 10 October 1979

Transients in the Vibrational Excitation of Cyclobutane Decomposition Using the Variable Encounter Method. M. C. Flowers, F. C. Wolters, B. D. Barton and B. S. Rabinovitch.

The probability of reaction of cyclobutane molecules in a fixed-time interval after experiencing a known number of collisions with a hot surface at temperatures between 749 K and 1126 K was determined using the Variable Encounter Method. Calculations utilizing exponential or gaussian models for energy transfer enabled the average amounts of energy transferred for deactivating collisions, $<\Delta E'>$, to be estimated. The exponential model fits the experimental data best and, using this model, $<\Delta E'>$ is 2430 cm^{-1} at 748 K and decreases to 1470 cm^{-1} at 1123 K. Surface collisions are more efficient than binary gas collisions; but cyclobutane is a less efficient partner than cyclopropane-d$_2$ (TR No. 11). The results follow from a quasi-statistical model of energy accommodation.

14. Technical Report TR14, 1 December 1979

A Crucial Demonstration of Strong Collisional Behavior of Vibrational Energy for Gas-Surface Collisions. M. C. Flowers, F. C. Wolters, D. F. Kelley and B. S. Rabinovitch.

Application of the VEM technique was made to the thermal cyclobutene decomposition system. Vibrational energy transfer in the cyclobutene - seasoned quartz surface system was studied. Collisional efficiency again declines with rise of temperature, but the occurence of strong collisions was demonstrated in crucial manner at temperatures below 450 K. The wall appears to behave like a theoretical strong collider below 450 K. This is a very novel finding.

15. Technical Report TR15, 31 March 1980

Gas-Surface Vibrational Energy Transfer in the Transient Region of a Low-Pressure Unimolecular Reaction. B. D. Barton, D. F. Kelley and B. S. Rabinovitch.

The Variable Encounter Method, for the study of gas-wall vibrational energy transfer in the transient region of a unimolecular reaction was applied to the

isomerization of cyclopropane to propylene. Temperatures in the range
900 K - 1125 K were employed. The average probability of reaction per
collision, $\bar{P}_c(m)$, was deduced from the data and compared with a theoreti-
cal stochastic calculation based on both gaussian and exponential models
for the energy transfer probabilities. The former model is more appropriate.
The efficiency of a seasoned quartz wall was greater than gas-gas collisions
of substrate and the efficiency declined with increase of temperature. The
steady state is closely approached (90%) in a comparatively small number of
gas-wall collisions — 10-20, approximately. The efficiency of transfer by
cyclopropane is comparable with that by cyclopropane-d_2 (TR 11).

The following were submitted in the present report period.

16. Technical Report TR16, 1 August 1980

   Collisional Relaxation of Vibrational Energy Transients in the Methyl
   Cyclopropane System. D. F. Kelley, T. Kasai and B. S. Rabinovitch.

The variable encounter method has been used to study vibrational energy
transients in the isomerization of methylcyclopropane to various butenes.
This molecule, which has a hindered methyl rotation mode, has the highest
vibrational energy level density of any molecule — cyclopropane, cyclobutene,
cyclobutane — that has been studied so far in testing the variation of energy
transfer efficiency with molecular structure. This system was studied with
reactor surface temperatures of 800 to 1130 K and average numbers of colli-
sions per encounter with the reactor of 5.6 and 20.0. An exponential model
of energy transfer was found to give the best fit to the data with the average
down step energy $<\Delta E'>$ decreasing from 1860 to 1415 cm^{-1} with increase of
temperature over the range studied. Incubation times increased from 14 to 19
collisions with increase in temperature, and these times, together with
values of the conventional relative collision efficiency β and values of
$<\Delta E'>$, are compared with those of other molecules studied by VEM. The calcu-
lated transient population distributions and the associated sequential reaction
probabilities are also displayed. The energy transfer efficiency from the
hot molecules in down-collisions is lowest in this system and hence the
weakest model — exponential — gives a good fit. By contrast, the efficiency
of up-transitions, i.e., energy transfer into the cold molecule measured in
this work is higher than for other molecules. This is a consequence of the
increased

eigenstate density and the important conclusion is reached that this verifies the suitability of a statistical model of energy accommodation to describe vibrational energy transfer involving high energy polyatomic molecules at these temperatures.

17. Technical Report TR17, 15 September 1980

A Reinvestigation of Transients in the Cyclopropane System by the Variable Encounter Method. M. C. Flowers, F. C. Wolters, D. F. Kelley and B. S. Rabinovitch.

The isomerization of cyclopropane to propene was reinvestigated under conditions identical to those used in a previously reported VEM study on cyclobutane. The simultaneous reaction of cyclobutane was also studied in the largest reactor. Some details of the method are amplified; the distribution functions for numbers of collisions in each reactor are displayed as are the contributions to reaction R(n) as a function of the number of consecutive collision n. The present data are in essential agreement with those obtained by Kelley et al [TR 11], although the average size of an internal energy down transition ($<\Delta E'>$) for cyclopropane molecules colliding with a hot surface is a little lower than previously estimated. The increasing efficiency of the surface in deactivating energized molecules as the surface temperature decreases is confirmed $<\Delta E'> = 2550$ cm^{-1} at 900 K, on a gaussian model for energy transfer, and $<\Delta E'> = 2000$ cm^{-1} at $\sim$ 1100 K). The surface acts as a somewhat stronger collider for cyclopropane than for cyclobutane and is also a more efficient collider for cyclopropane than are gas-gas cyclopropane collisions. This accords with the results of TR16 and leads to the important conclusion that heterogeneous collision is more efficient than homogeneous collision, in general, for the deactivation of excited molecules.

18. Technical Report TR18, 15 October 1980

Transients in Thermal Isomerization of Cyclobutene by the Variable Encounter. Vibrational Energy Transfer and Relaxation at Lower Temperatures. F. C. Wolters, M. C. Flowers and B. S. Rabinovitch.

Vibrational energy transfer and relaxation in the thermal isomerization of cyclobutene to 1,3-butadiene was studied over the temperature range 429 K - 778 K using the Variable Encounter Method. Reactors characterized by various mean number of collisions, m , per encounter of a substrate molecule with the reactor (m = 2.6, 5.9, 8.5 and 27.2) were used. The

significant observation was made that strong collider behavior in colli-
sions of substrate with a seasoned fused quartz wall is reached at lower
temperatures (below 450 K), as evidenced by the coincidence of values of
the probability of reaction per collision, $\bar{P}_c(m)$, obtained in VEM reactors
having different m values. The average energy transferred to the wall per
deactivating collision, $<\Delta E'>$, increased strongly as temperature decreased,
from $<\Delta E'> = 2150$ cm^{-1} at 764 K to > 6000 cm^{-1} at 460 K. Various forms of
models for the probability of energy transfer in down transitions were
applied to data. The weak form — exponential — cannot apply, in contrast
to the behavior that applies at higher temperatures for looser molecules
(higher vibrational eigenstate densities) such as methyl cyclopropane (TR16).

19. Technical Report TR19, 15 March 1981.
    Energy Transfer at High Temperatures in the Cyclopropane System.
    Temperature Dependence of $<\Delta E'>$. T. Kasai, D. F. Kelley and B. S.
    Rabinovitch.

The study of collisional energy transfer between cyclopropane molecules
and a seasoned silica wall by the Variable Encounter Method was extended
over a range of more than 500° upward in temperature to 1325 K. The value
of $<\Delta E'>$, the average energy of a down-transition upon collision of the hot
substrate molecule with the wall to decrease monotonically. The data pro-
vide the most accurate and well-documented display for a polyatomic molecule
of the temperature trend of $<\Delta E'>$ presently available. The rate of decrease
in $<\Delta E'>$ seems to be more rapid at lower temperatures. The data have been
explained by the theory of Lin and Rabinovitch on a quasi-statistical accommo-
dation model.

The behavior at still higher temperatures is considered to be not well
known and must be considered as in quite unsatisfactory condition. It is of
extreme practical and theoretical importance to detect the possible transi-
tion of the observed behavior from an attractive potential-dominated accommo-
dation phenomenon to a Landau-Teller type repulsive potential-dominated
impulsive phenomenon.

20. Technical Report TR20

Single-Collision Gas-Surface Vibrational Energy Transfer in a
Reacting System. D. F. Kelley, T. Kasai and B. S. Rabinovitch.

Gas-surface vibrational energy accommodation in a reactive system has
been studied under <u>single collision</u> conditions for the first time for
polyatomic molecules. The reaction system was the isomerization of cyclo-
butene to 1,3-butadiene. Both seasoned pyrex and silica surfaces were
used over the temperature ranges 400-775 K and 500-975 K, respectively.
Strong collider behavior was observed below $\sim$ 425 K. The vibrational
energy accommodation coefficient was found to decrease with rise of
temperature from $\sim$ 1.0 to 0.2, while the relative collisional efficiency
β_1 declined from $\sim$ 1.0 to 0.008. A stochastic calculation was used to fit
the data. This technique provides a more sensitive test between the various
model forms for energy transfer than has been possible heretofor. It is
clearly shown that a Gaussian or particularly a Boltzmann weighted exponen-
tial form provide the best fit.

III. Listing of Publications.

1. Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures, Proceed. Tenth Internat. Shock Tube Sympos. ed. G. Kamimoto, Kyoto, 1976.

2. Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems. D. C. Tardy and B. S. Rabinovitch, Chem. Revs. 77, 369 (1977).

3. On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations, S. E. Stein and B. S. Rabinovitch, Chem. Phys. Lett. 49, 183 (1977).

4. Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems. I. Oref and B. S. Rabinovitch, Chem. Phys. 26, 385 (1977).

5. Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method, D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch, J. Phys. Chem. 82, 355 (1978).

6. Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane. E. Kamaratos, J. F. Burkhalter, D. G. Keil and B. S. Rabinovitch, J. Phys. Chem. 83, 984 (1979).

7. Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically? I. Oref and B. S. Rabinovitch, Accts. Chem. Res. 12, 166 (1979).

8. Collisional Relaxation of Non-equilibrium Vibrational Energy Distributions in a Thermal System. Surface Collisions, D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch, J. Chem. Phys. 71, 538 (1979).

9. Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures by Variable Encounter Method. M. C. Flowers, B. D. Barton, F. C. Wolters and B. S. Rabinovitch. Am. Soc. Mass. Spectrom. Proceedings, ed. A. E. Harrison, 27, 661 (1979).

10. Collisional Relaxation of Transient Vibrational Energy Distributions in a Thermal Unimolecular System. The Variable Encounter Method. D. F. Kelley, L. Zalotai, and B. S. Rabinovitch. Chem. Phys. 46, 379 (1980).

11. Vibrational Energy Transfer in a Diffusion-Flow Cyclopropane-d_2 System. J. F. Burkhalter, E. Kamaratos, and B. S. Rabinovitch, J. Phys. Chem. 84 (1980) 476.

12. A Crucial Demonstration of Strong Collisional Behavior of Vibrational Energy for Gas-Surface Collisions. M. C. Flowers, F. C. Wolters, D. F. Kelley and B. S. Rabinovitch, Chem. Phys. Lett. 69, 543 (1980).

13. Transients in the Vibrational Excitation of Cyclobutane Decomposition Using the Variable Encounter Method. M. C. Flowers, F. C. Wolters, B. D. Barton and B. S. Rabinovitch, Chem. Phys. 47 (1980) 189.

14. Gas-Surface Vibrational Energy Transfer in the Transient Region of a Low-Pressure Unimolecular Reaction. B. D. Barton, D. F. Kelley, and B. S. Rabinovitch. J. Phys. Chem. 84, 1299 (1980).

15. Collisional relaxation of vibrational energy transients in the methyl-cyclopropane system. A variable encounter method study. D. F. Kelley, T. Kasai and B. S. Rabinovitch, <u>73</u>, 5611 (1980).

16. Transients in Thermal Isomerization of Cyclobutene by VEM. Vibrational Energy Transfer and Relaxation at Lower Temperatures. J. Phys. Chem. 85 (1981) 589.

17. Surface-Gas Energy Transfer in the Cyclopropane/Cyclobutane Isomerization Systems by the Variable Encounter Method. M. C. Flowers, F. C. Wolters, D. F. Kelley, and B. S. Rabinovitch, J. Phys. Chem. 85 (1981) 849.

18. Single-Collision Gas-Surface Vibrational Energy Transfer in a Reacting System, D. F. Kelley, T. Kasai and B. S. Rabinovitch. J. Phys. Chem. 85 (1981) 1100.

19. Energy Transfer at High Temperatures in the Cyclopropane System. Temperature Dependence of $<\Delta E'>$. T. Kasai, D. F. Kelley and B. S. Rabinovitch, Chem. Phys. Lett., in press.

IV. Current Work

The following work has been completed (but reports have not yet been circulated), or is in progress.

1. <u>Molecular Structure Effects</u>. A study by VEM of n-propyliodide has been completed. The purpose of the study was to extend the test of the relation between molecular structure and energy transfer efficiency. Propyl iodide is the first polar molecule to be studied in this series. The interesting result has been found that although the vibrational energy level density is greater than that in cyclopropane so that lesser efficiency would be expected, instead the energy transfer model is a stronger one and is attributed to increased attractive intermolecular potential. This will be described in TR21.

2. <u>Nitroalkanes</u>. We are in the middle of a study of the decomposition of nitromethane by the VEM technique. We are using m = 5 and 14. We have determined the average collisional reaction probabilities $P_c(m)$. The reaction may be influenced by surface, and this is taking time and effort to sort out. Also, with our comparatively mild sequential activation technique, we have been able to detect at least one higher molecular weight intermediate that has not hitherto been detected in a thermal system.

3. <u>Isotopic Substitution</u>. A study of the secondary molecular isotope effect on efficiency of vibrational energy transfer at high temperatures is nearing completion. The comparison of <u>cyclo-C_3H_6</u> and <u>cyclo-C_3D_6</u> provides a very refined test of the relationship between transfer efficiency and molecular structure.

4. <u>Variation of Initial Vibrational Distribution</u>. The study of vibrational energy transfer efficiency as a function of the initial vibrational population vector has not been studied previously for polyatomic molecules/thermal systems. We are completing a study of the isomerization of cyclobutene over the range of reaction temperatures from 600 K to 900 K and initial population temperatures from 273 K to 600 K.

V. Future Work.

The following studies are planned in the year ahead:

1. Nitroalkanes. The study of the vibrational collisional energy transfer efficiency with nitromethane will be continued. This molecule has a large dipole moment and appears to show high efficiency in our preliminary work. The biggest complication in this study may be catalytic effects, but this will, hopefully, not prevent us from reaching a successful analysis of the data. Past work between 800 K and 1000 K will be extended. Other nitroalkanes will also be considered.

2. Initial Energy Distribution. We will complete the present investigation of changing initial temperature (average vibrational energy) of the cyclo-butene species on the energy transfer process. We will then extend the work to a molecule having a higher vibrational level density pattern such as methyl cyclobutene.

3. Surface Variation. We hope to examine the effect of variation of the nature of the wall surface and propose to investigate next a metal (gold) surface. We have hoped to initiate this work earlier but were held off by the other work in progress.

4. Variation of Molecule Parameters. We should like to move part of the work to the study of inorganic species such as $NOCl$, NO_2Cl, etc. as examples of plausible candidates. This would widen the scope of this aspect of the study considerably. Virtually no studies of the kind we propose have ever been made.

VI. Personnel

The following graduate students and fellows have been involved on this project in the period.

Dr. Ryuichi Arakawa
Prof. K. J. Chao (Sabbatical visitor, Tsing Hua University, Taiwan)
Dr. Toshio Kasai
Dr. David Kelley
Reiko Tosa
Wei Yuan (Sabbatical visitor, Qinghua University, Peking)

ENERGETIC MATERIALS RESEARCH

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